IONIZATION BY POSITIVE IONS

THE question as to whether positive ions can ionize atoms has been the subject of much controversy. Experimentally no direct evidence exists which will enable one to decide between the two apparently opposing views held. If one regards the phenomenon from the point of view of the ionization of an atom by a moving charged particle in virtue of the action of the charge on the electron of the neutral atom, one must agree with J. J. Thomson[1] that it is unlikely that on this mechanism ions with less than a few thousand volts equivalent of energy can ionize. On the other hand, as J. Franck[2] points out, and as is indicated by certain phenomena in ionization by slow canal rays, in the discharge of electricity from positively charged points, and from the temperature ionization observed by King,[3] and also by Noyes and Wilson,[4] we have definite evidence of the ionization of gases by impact between charged or uncharged atomic masses moving with velocities corresponding to only two or three times the ionizing energy. These two apparently contradictory[5,1,2] views, together with the conflicting experimental evidence put forward in an attempt to decide the question, have led to a good deal of confusion. In part this has been clarified by Joos and Kulenkampff[30] but not completely. In a seminar course the writer recently had the opportunity of reviewing the literature on the subject and with the benefit of the criticisms of his two colleagues, Professor R. B. Brode and Dr. Arthur von Hippel, believes that he has been able to clarify the situation still more and that he has been able to show that there is no real contradiction in the two views.

It is the purpose of this article to briefly set forth these conclusions. To do this we may regard three distinct processes. They are:

1. The ionization by *rapidly* moving *charged* particles, *e.g.,* electrons, protons, and doubly charged He atoms.*

2. The ionization of molecules of a gas of lower or equal ionizing potential by ionized atoms or molecules which may be in motion or at rest (*e.g.,* an exchange of charge).

3. The ionization resulting from the impact of atoms or molecules, charged or neutral, which possess electrons and which have an energy which is a small multiple of the ionizing energy of one of the atoms.

1. The first class of ionizing processes is characterized and governed by the classical laws of electrodynamics and the laws of momentum and energy[6,7] with the limitation that energy transfer to an electron of an atom acted on must follow the quantum conditions, [8,9,10] (*i.e.,* energy can only be absorbed if the electron in question receives a quantum of energy demanded by its change in status). The applications of these laws to the fast electron, the proton and the alpha particle, have been adequately proven by the agreement in order of magnitude between the predicted results and observations. That is, the ionization by electrons (Whiddington's[7,11] law and possibly even the application to ionization for slower electrons, though the latter is more doubtful), by protons[12] and by α particles as calculated by Henderson,[8] Fowler,[9] Bohr[7] and others, agrees within a factor of two or three with the observations. These laws, as Thomson[1] points out, demand that ionization by such particles in virtue of the action of the charge ceases at velocities easily computed from laws of momentum and energy, corresponding to values of the order $5\times10^7-1\times10^8$ cm/sec. Such velocities correspond to energies of the order of the ionizing potentials for atoms in the case of electrons, to energies of the order of 2,000–3,000 volts for protons, and to energies of the order of 10,000 volts for alpha particles. The efficiency of this type of ionizing action is very high and is more or less successfully predicted from classical theory, assuming the ionization potentials as observed to be correct.[7,8,9,10] The conclusions are substantiated by the sudden cessation of ionization by α particles and protons[13] at the end of their range observed, and by the recent work of Dempster[14,5] on the long free paths of protons of 900 volts velocity. It is the only process by which such single charges can produce ionization.

2. The second class of phenomena belong, properly speaking, in that class of phenomena called "inelastic

1 Thomson, J. J., *Phil. Mag.* 48, 1, 1924; and also 23, 454, 1912.

2 Franck, J., *Zeits. f. Phys.* 25, 312, 1924; *Handbuch der Physik.* Vol. 23, p. 731.

3 King, A. S., *Astrophys. J.* 48, 13, 1918, and many other papers in this journal.

4 Noyes and Wilson, *Astrophys. J.* 57, 20, 1923.

5 Rüchardt, E., *Handbuch der Physik,* Vol. 24, p. 99.

* Singly charged He atoms and all *rapidly* moving charged particles should be included here. As, however, these carriers also can act to ionize in other ways which confuse the issue, and in order to emphasize the mechanism of the process, these have been purposely left out as typical examples of this class.

6 Thomson, J. J., *Phil. Mag.* 23, 449, 1912, "Conduction of Electricity through Gases," pp. 370–382.

7 Bohr, N., *Phil. Mag.* 25, 10, 1913, and also 30, 581, 1915.

8 Henderson, G. A., *Phil. Mag.* 44, 680, 1922.

9 Fowler, R. H., Proc. Camb. Phil. Soc. 21, 521, 1923.

10 Loeb and Condon, *Jr. Frank. Inst.* 200, 595, 1925.

11 Whiddington, R., Proc. Roy. Soc. 85A, 323, 1911; also 86A, 360, 1912.

12 Dempster, A. J., *Phys. Rev.* 8, 656, 1916.

13 Baerwald, H., *Ann. der Phys.* 65, 167, 1921.

14 Dempster, A. J., Proc. Nat. Acad. Sci. 11, 552, 1925; also 12, 96, 1926; *Phil. Mag.* 3, 115, 1927.

impacts of the second class," first discovered experimentally by Franck[15] and Cario, and later observed directly by Erikson[16] and Harnwell.[17]

They explain many of the phenomena observed by Dempster[12] on canal rays of low velocity. They occur fairly readily, and are largely independent of the velocity of the carrier. It is, however, possible that through the third class of ionizing phenomena the energy of motion could be utilized to make this group include ionization by moving ions of appropriate velocity of molecules of higher ionizing potential. To date, however, no certain evidence exists for this extension, though from indirect observation it seems probable. This process obviously can not lead to the production of a very much larger number of charged carriers than the initial number of charged carriers. Thus in a great many problems of ionization by means of charged particles their importance is secondary.

3. The third class of processes are definitely established by the existence of temperature ionization observed by King[3] and treated theoretically exhaustively by Eggert,[18] by Saha,[19] and Fowler.[20] Even if some of the assumed quantities (*e.g.*, the energies of the atoms necessary for ionization in such a process) in the equations turn out to be in error by a factor of two or three, the correctness of the deduction is unquestioned. As regards other evidence for ionization of gas molecules by positive ions, or moving neutral molecules of relatively low velocities, the evidence is less clear if one exclude occurrences of the type of Class 2 above.[12] The evidence from direct measurement on positive rays has been seriously questioned by Horton and Davies[21] and by Hooper,[22] due to the fact that secondary emission of electrons from the walls through the positive ion bombardment and photoelectric phenomena were not rigorously excluded. The work of Baerwald and others[23] on emission of secondary electrons from metals by positive ion bombardment upholds this. Hooper concludes that if ionization of a gas by positive ions below 1,000 volts occurs, the process is very inefficient. He believes that at high pressures (where many collisions can take place and the ionization could be observed for inefficient agencies) there is some evidence that it occurs in his experiments. The evidence from the experiments on ionization phenomena in gases and sparking potentials in fairly uniform fields, as interpreted by Townsend,[24] has recently been seriously called into question[25,26] on the basis of the probable actions of positive ions or radiation on the cathode. Townsend[27] himself agrees that such processes would fit his equations as well as experimental uncertainty admits. He however points out that only by assuming ionization by positive ions of low velocity in a gas can we explain the discharge from positive points at high potentials.[28,29] In this assertion he is undoubtedly correct if we add the possibility that such ionization may be in part indirect as later described. There is thus evidence that neutral atoms, molecules, canal rays, and *slowly* moving positive rays directly or indirectly can ionize gas molecules by impact, though the efficiency of the process is obviously very low. This type of activity is, however, essentially different from that under Class 1 in *that it is independent of the charged state of the ionizing atom or molecule, so that the charge is but incidental to the mechanism.* The process, however, depends on one additional feature. *Every atom ionizing in this fashion must have at least one electron in an orbit about it, and possibly more.*

It is in fact the presence of the electrons in these ionizing systems that enables them to produce ionization independently of charge, and thus give a mechanism which can be clearly differentiated from the first class of ionization. With electrons in each of the atoms or systems colliding, transfers of energy between the electrons of the two systems again become possible at low velocities. However, it is difficult to postulate the exact mechanism of such transfers, in which the relative energies of two atoms are transferred to one or two of their electrons in a molecular impact. To date the new quantum mechanics has been unable to cope with the problem. The earlier discussions of Franck,[1] and Joos and Kulenkampff[30] treated the atoms as elastic spheres. If one could conceive of the electrons being rigidly held in stationary positions by the binding forces of the nucleus, interactions of the observed sort might be expected. Such an assumption enables one to find a plausible explanation for inefficiency of the process; for it would be a relatively rare atomic encounter that brought two electrons of the colliding atoms into such

15 Franck and Cario, *Zeits. für Phys.* 11, 3, 1922.
16 Erikson, H. A., *Phys. Rev.* 28, 372, 1926.
17 Harnwell, G. P., *Phys. Rev.* 29, 830, 1927.
18 Eggert, J., *Phys. Zeits.* 20, 570, 1919.
19 Saha, M. N., *Phil. Mag.* 40, 478, 1920.
20 Fowler, R. H., *Phil. Mag.* 45, 1, 1923.
21 Horton and Davies, Proc. Roy. Soc. 95A, 333, 1919.
22 Hooper, W. J., *Jr. Frank Inst.* 201, 311, 1926.
23 Rüchardt, E., *Handbuch der Physik,* Vol. 24, p. 105.
24 Townsend, J. S., "Electricity in Gases," Chap. IX, p. 322.
25 Holst and Oosterhuis, *Phil. Mag.* 46, 1117, 1923.
26 Taylor, James, *Phil. Mag.* 3, 753, 1927; also 4, 505, 1927, Proc. Roy. Soc. 114A, 73, 1927.
27 Townsend, J. S., "Electricity in Gases," p. 330.
28 Huxley, H. G. L., *Phil. Mag.* 3, 1057, 1927.
29 Townsend, J. S., "Electricity in Gases," p. 371.
30 Joos and Kulenkampff, *Phys. Zeits.* 25, 257, 1924.

a relation that the energy of atomic motion was concentrated on one electron and thus made possible its escape. However, the electrons are more probably in orbits in the atoms and the flexibility of this type of binding, coupled with the experimentally observed fact that the orbital momentum of electrons in atoms is not manifested in ionization processes,[31] makes it difficult, if not impossible, to explain the facts in a simple mechanical fashion. We can only conclude that there exists a mechanism in atoms which in *rare collisions by means of the interactions of the electrons in the atoms enables the relative energy of the atoms to be transferred to one of the electrons.*

The presence of a positive charge on one of the two colliding atoms at low velocities should affect the ionization by such a mechanism but slightly. As Franck[1] has stated it increases the energy necessary to cause ionization, as with the charged atom the electron must escape against an attractive charge of two units instead of one. Besides this minor influence the charge plays an important indirect rôle, in low velocity phenomena, in that it enables a molecule or atom to acquire its ionizing energy from an electrical field, an energy which it otherwise would practically never acquire at room temperatures as a result of the heat motions. Such an atom or molecule having acquired the energy through its charge is then able to ionize molecules itself, or perhaps is able by impact to impart its energy to a neutral molecule which can ionize slightly more effectively. In any case whatever its manner of producing ions, the function of the charge is but indirect enabling the ion *to acquire energy. It has little to do with the subsequent mechanism of removal of electrons* by the ion, thus clearly differentiating its ionizing mechanism from that of swiftly moving charged particles.

It is also conceivable that one ion may ionize by any two or even all three mechanisms simultaneously, although at high speeds the preponderating mechanism for an ion with electrons will be processes of Class 1, while as it slows down the processes of Class 2 and 3 will entirely predominate. At intermediate speeds probably all mechanisms are active and thus lead to some of the apparently contradictory results obtained.

We thus see that in terms of the three different mechanisms, the outstanding conflicting observations can be simply explained and it is seen that there is no essential contradiction even between the extreme views of Thomson and Franck; for we have seen that neither a proton nor a doubly charged helium atom can ionize below certain minimum velocities as classical theory demands that they should not, while hydrogen atoms, singly charged helium atoms and neutral helium atoms can be expected to ionize at low velocities albeit very ineffectively.

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[31] Watson, E. C., *Phys. Rev.* 30, 479, 1927.

SPECIAL ARTICLES

CORRELATION BETWEEN ELECTROMOTIVE SERIES AND OXIDATION POTENTIALS AND PLANT AND ANIMAL NUTRITION

IN studying the distribution and the dominance of pasture plants, it was observed that there is a definite correlation between the dominance of certain pasture plants and the natural or native vegetation. An attempt was made to correlate the growth and dominance of the various plants with the soil acidity, but it was soon found that there is no very close correlation between acidity of the soil and the dominance of certain types of pasture plants.

Since no very definite correlation was found between the acidity of the soil and the growth and dominance of certain plants, an attempt was made to correlate plant growth with plant residues, particularly the basic nitrogenous materials, including ammonia, amines, etc., and here again only a partial correlation was found between the availability of the basic nitrogenous organic residues and plant growth.

The nitrogen carbon ratio in the organic residues probably affects the mobility of the nitrogen in the soil. There is a difference in the nitrogen carbon ratio in various plant residues. The difference in the nitrogen carbon ratio in peat soils illustrates the points in question. It has been found that some peat soils have a nitrogen carbon ratio as narrow as 1: 8, while others have a ratio as wide as 1: 70 or wider. This difference in nitrogen carbon ratio undoubtedly affects the availability of anionic nitrogen. It has been found that there is a close correlation between the calcium oxide content and the width of the nitrogen carbon ratio in peat soils. Where the nitrogen carbon ratio is narrow, it indicates that there is a relatively large amount of high oxidation potential mineral basic material present. And in such a situation it has been found that there is often an accumulation of toxic amounts of nitrates. But when the nitrogen carbon ratio is wide it indicates that there is a limited amount of high oxidation potential mineral basic material present. And where such a condition prevails it may result in a prolonged nitrogen starvation period, especially early in the growing season. Where the nitrogen carbon ratio is very wide such plants as some of the conifers, poverty grass (*Danthonia spicata*), certain species of Agrostis, etc., which may readily utilize cationic nitrogen, are apt to dominate in nature. Other plants, such as certain species of oak, hickory, poa, etc., seem